CONFOCAL RAMAN MICROPROBE AND IR REFLECTANCE STUDY OF MINERALS IN THE MARTIAN METEORITE ALH84001.

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INTRODUCTION. Since the original claim of possible evidence of ancient life in the carbonate globules of the martian meteorite ALH84001 [1], there has been some controversy regarding alternative explanations for the origin of these carbonates. The proposed alternatives to biochemical formation include high-temperature hydrothermal [2,3] or vapor-phase [4] precipitation, low-temperature fluid-mediated precipitation [5,6] or replacement of maskelynite [7] or shock melting [8]. To resolve the controversy, additional mineralogical structural information needs to be considered together with the current body of petrographic and geochemical data.

Micro-Raman spectroscopy has been used extensively for inter-atomic structural studies in mineralogy and earth science [9], because of its excellent spectral fingerprinting capabilities. Furthermore, infrared (IR) reflectance studies can provide complementary vibrational information. Taken together, the micro-Raman and IR reflectance techniques can non-desctructively provide important data on phase identification, degree of order, and degree of hydration of minerals in meteoritic thin sections.

EXPERIMENTAL. Confocal micro-Raman and Fourier-Transform infrared (IR) reflectance spectra were obtained from minerals (silica, carbonates, and phosphates) in two thin sections (,6 and ,146) of ALH84001. Chosen mineral grains had previously been identified petrographically and analyzed by electron microprobe. For comparison, reference Raman spectra of the microscope slide and mounting epoxy in each thin section were also recorded. The confocal micro-Raman system used in this work has been described elsewhere [10]. Infrared reflectance spectra were obtained with a Spectra-Tech IR-Plan microscope interfaced to a Bomem DA3

Fourier Transform Infrared spectrometer equipped with a KBr beam splitter, and a liquid-nitrogen-cooled MCT detector. Analyses were obtained from circular 100 μm diameter regions on the sample by inserting a 1 mm pinhole in the image plane at the top of the microscope. Reflectance spectra were referenced to a gold foil standard. Although the spectrograph (IR source, beam splitter and detector) was kept under vacuum, the segment of the optical path encompassing the microscope was open to air.

RESULTS AND DISCUSSION. Silica is a scattered accessory in ALH84001, although the specific phase has not been reported. Figure 1 shows the confocal micro-Raman spectrum of a silica bleb (associated with plagioclase glass) in an inter-grain boundary of ALH84001,6 together with spectra of the glass slide and of synthetic silica glass. Apart from a weak, sharp peak at 462 cm^{-1} attributable to a minor proportion of crystalline quartz, the silica spectrum shows broad features consistent with an amorphous phase (Fig. 1). Silica is an important indicator of the degree of shock metamorphism [11]. By comparison with previous Raman study on laboratory shocked quartz, the Raman spectrum of silica in ALH84001,6 shows this mineral has been subjected to peak shock pressures above 31 GPa [12].

Figure 2 shows a comparison between IR reflectance spectra of two phosphate phases, indentified on the basis of electron microprobe analyses as chloroapatite and a Mg-bearing Ca-phosphate, which occur intergrown within a pyroxene inter-grain boundary in ALH84001,6. The identification of the second phase as merrillite (β-Ca-phosphate structure) is made by comparing its IR spectrum (Fig. 2) and its Raman spectrum to those of synthetic phosphates having the
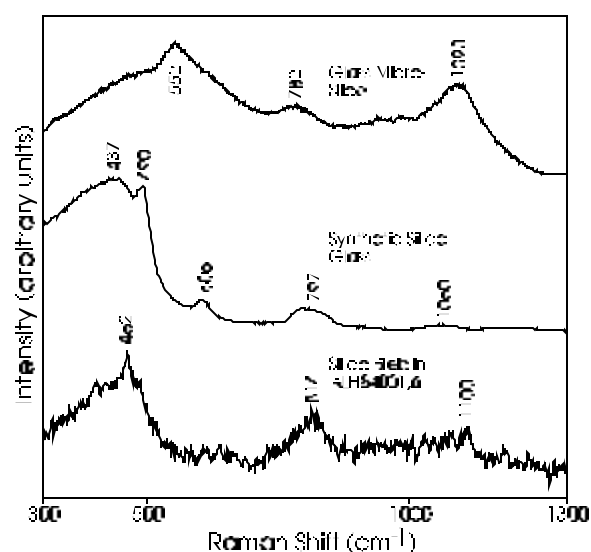

Fig. 1. Confocal micro-Raman spectra of silica bleb in ALH84001,6 (lower curve), thin section microscope slide (upper), and silica glass (middle).
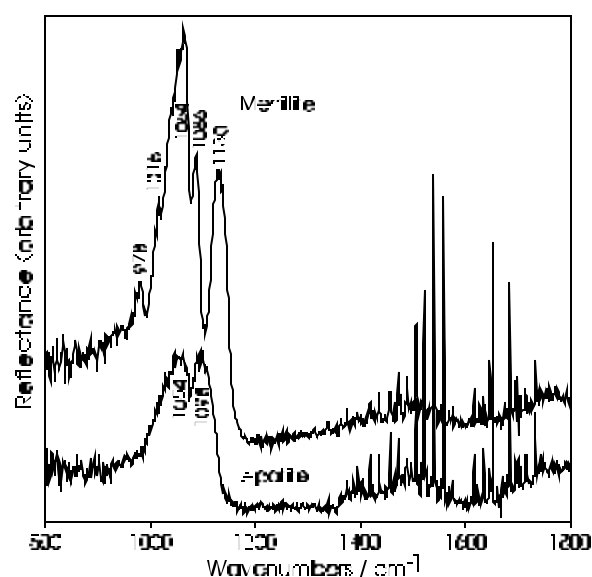

Fig. 2. Infrared reflectance spectra of intergrown phosphates in an inter-grain boundary of ALH84001,6.

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β-$Ca_3(PO_4)_2$ structure [13,14]. The structure of anhydrous merrillite (known from the moon and chondritic meteorites) is different from that of whitlockite (terrestrial), which preferentially incorporates water [15]. The medium intensity band at 978 cm^{-1} in the upper spectrum originates from the ν_1 symmetric stretching mode of PO_4^{3-} ions [16] and the bands in the 1000-1150 cm^{-1} region of both spectra (Fig. 2) result from antisymmetric ν_3 vibrations [13]. Sharp peaks between approximately 1400 and 1700 cm^{-1} result from atmospheric water in the microscope optical path. Additional weak, broad features underlying these sharp peaks in both spectra are attributed to combinations between the ν_1 and the ν_3 and ν_2 PO_4 modes [13] and not from bound OH. The Raman spectrum of apatite in ALH84001,6 shows no evidence of the OH^- librational band at 655 cm^{-1} characteristic of hydroxyapatite [16]. Also absent, from the Raman spectrum of intergrown merrillite, is any indication of the P-OH stretching band which occurs at 923 cm^{-1} in spectra of terrestrial whitlockite [17]. Together, these data indicate that the ALH84001 phosphates are essentially anhydrous.

Figure 3 shows confocal micro-Raman spectra (low wavenumber region) of carbonates in both the Mg-rich mantle and CaFe-enriched core of an irregular carbonate patch in ALH84001 and comparisons with spectra of terrestrial carbonates. The Raman modes shown in Fig. 3 include two lattice modes (librational and translational) below 345 cm^{-1} and the ν_4 (in-plane bend) mode near 730 cm^{-1} [18]. In accordance with electron microprobe analyses, the band positions in the Raman spectrum of the mantle region are similar to those of pure magnesite and those of the core are significantly shifted towards lower wavenumbers. However, the bandwidths of the meteoritic carbonate are significantly broader than their terrestrial counterparts. The Raman spectrum of the core of the meteoritic carbonate (Fig. 3, lower) also exhibits an unusual broad band near 674 cm^{-1} which may be correlative with a band near 506 cm^{-1} in the siderite Raman spectrum (Fig. 3). Similar bands were exhibited but not discussed [19]

in the spectra of siderite and rhodochrosite ($MnCO_3$) and we speculate that they may represent magnon bands.

Part of the disagreement concerning the origin of ALH84001 carbonates relates to their unusual compositional trend across a miscibility gap and the related question of possible sub-microscopic phase separation [6]. To test this question, one can construct a synthetic Raman spectrum representing the expected results (in the vicinity of 300 cm^{-1}) for a mechanical mixture of ferroan-dolomite and breunnerite using a representative carbonate core analysis ($Ca_{.19}Mg_{.47}Fe_{.34}CO_3$), the carbonate end member band positions [19], an assumption of linear band shift with composition in each solid solution series, and the observed bandwidth (14.3 cm^{-1}) of the 282 cm^{-1} band of siderite. This simulation yields two well-resolved Raman bands at 294 and 317 cm^{-1} as contrasted with the broad asymmetric band at 312 cm^{-1} in the spectrum from the core region of the ALH84001 carbonate (Fig. 3). We conclude that these carbonates are metastable single phases and not exsolved at a sub-micron scale. Similar band broadening has been observed in single-phase synthetic and biogenic magnesian calcites as a result of both cationic mixing disorder and anionic positional disorder (tilting of CO_3^{2-} ions out of the crystallographic basal plane) [20]. The lattice mode bandwidths of biogenic magnesian calcites are greater and more variable than those of synthetic carbonates of similar composition because of greater positional disorder [20]. Carbonate lattice mode vibrations in ALH84001 are also broad and variable (Fig. 3) but further experimental control studies (combining Raman, electron microprobe, and X-ray diffraction) on carbonates of appropriate composition and mode of origin will be required to properly interpret this effect.

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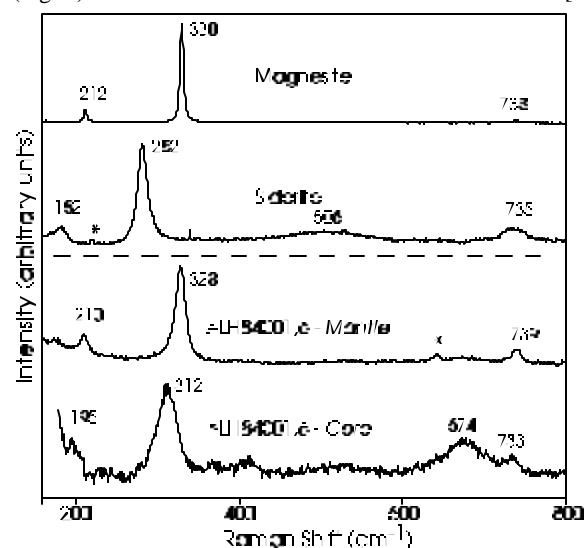

Fig. 3. Raman spectra of cleavage rhombs of terrestrial magnesite ($MgCO_3$) and siderite ($FeCO_3$) and of two spots in irregularly shaped carbonate in ALH84001.